



CRYSTAL STRUCTURE AND HIRSHFELD SURFACE ANALYSIS OF (Z)-2-PHENYL-4-((4,6,8-TRIMETHYLAZULEN-1- YL)METHYLENE)OXAZOL-5(4H)-ONE^{**/**}

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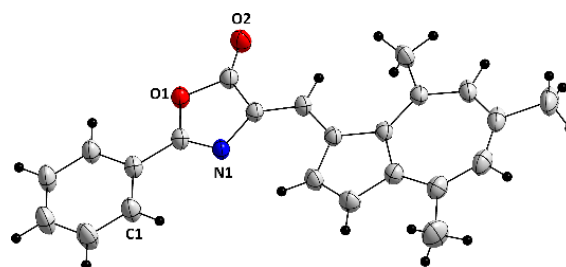
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The molecular structure of (Z)-2-phenyl-4-((4,6,8-trimethylazulen-1-yl)methylene)oxazol-5(4H)-one (**1**) was determined by single-crystal X-ray diffraction. The crystal presents a monoclinic crystal system, space group $P2_1/n$, $a = 7.0706(3)$ Å, $b = 18.7978(7)$ Å, $c = 13.7059(7)$ Å, $\beta = 103.013(5)^\circ$, $V = 1774.89(14)$ Å³. In the crystals of **1**, strong π - π stacking interactions are present, with an average distance of 3.54 Å between centroids.



INTRODUCTION

Azulene, a non-alternating aromatic hydrocarbon, exhibits low ionization energy, high electron mobility and less symmetric structure compared to naphthalene, its skeletal isomer. Thus, azulene derivatives are used as building blocks for the generation of materials with valuable technical properties.^{1–6} The exceptional structure of azulene with symmetrical electron distribution only with respect to the x-axis gives some special chemical and physical properties to compounds in which it is inserted compared to compounds that contain the

well-known naphthalene structure with additional negative charge symmetric about the y-axis.⁷

The study of organic push-pull systems has been an outstanding target due to their valuable technical properties such as nonlinear optical responses, electrochemical behavior, or coloring properties. Therefore, the past and also present interest for the study of these compounds is understandable due to their various applications in the technical field, as materials with nonlinear optical (NLO) properties⁷ and as potential host molecules in ligands for metal ion detectors.⁸ At the same time, several organic compounds

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** This paper is dedicated to the memory of Dr. Liviu Bîrzan.

*** Supplementary information on <https://www.icf.ro/rrch/> or <https://revroum.lew.ro/>

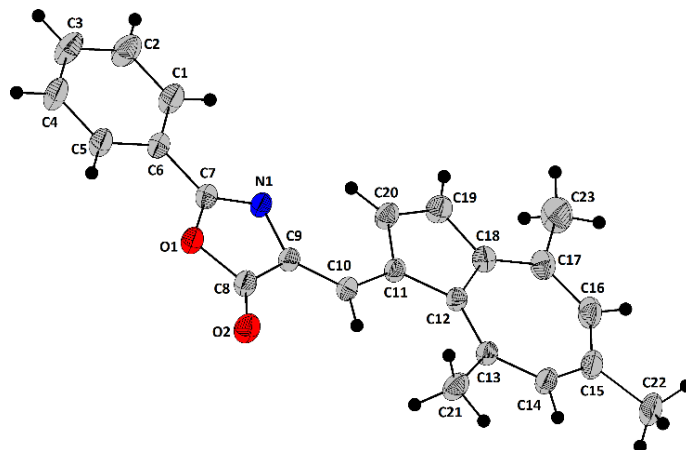


Fig. 1 – Thermal ellipsoid representation (25% probability) of the molecular structure of **1**. Selected bond lengths (Å) and angles (°): O1–C7 1.374(2), O1–C8 1.404(2), O2–C8 1.200(3), N1–C7 1.288(3), N1–C9 1.400(2), C6–C7 1.459(3), C9–C10 1.363(2), C10–C11 1.421(3); C7–O1–C8 105.05(15), C7–N1–C9 105.22(17), O1–C7–N1 116.22(17), O1–C7–C6 117.17(17), N1–C7–C6 126.61(18), O1–C8–C9 104.96(16), O2–C8–C9 134.03(18), N1–C9–C8 108.55(15), N1–C9–C10 129.07(18), C8–C9–C10 122.38(17), C9–C10–C11 128.46(18).

In the crystal, the molecules of **1** arrange in layers which are bonded *via* supramolecular $\pi\cdots\pi$ interactions established between azulene seven-membered aromatic ring and oxazolonic fragment (Fig. 2). The dihedral angles between the planes of the molecules involved in the $\pi\cdots\pi$ interactions are

very small [*e.g.*, $0.63(11)^\circ$ for the planes of the rings with Cg1 and Cg4ⁱ, or Cg4ⁱⁱ, respectively (*vide infra* Fig. 2 caption the definition of the centroids)], as well as ring slippages [*e.g.*, Cg1/Cg4ⁱ 0.840 Å, Cg1/Cg4ⁱⁱ 1.509 Å].

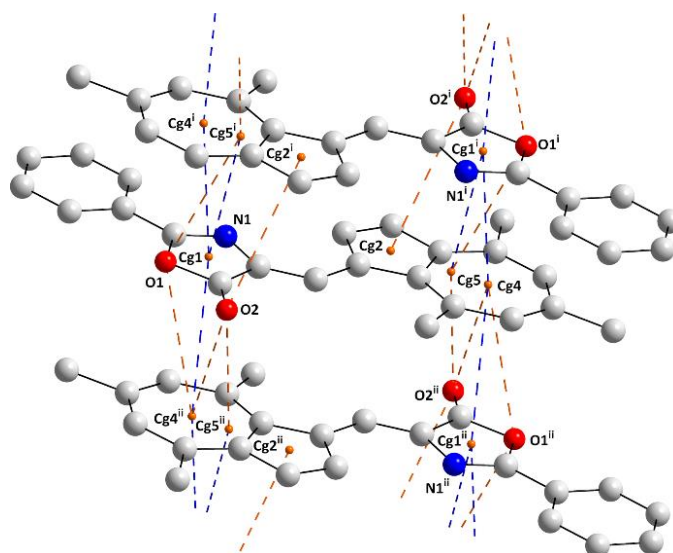


Fig. 2 – $\pi\cdots\pi$ interactions (blue) and C–O $\cdots\pi$ contacts (orange) in the crystals of **1**. Selected distances (Å) and angles (°): O2 \cdots Cg2ⁱ 3.924(2), C8–O2 \cdots Cg2ⁱ 68.59(14), C8 \cdots Cg2ⁱ 3.660(2); O2 \cdots Cg4ⁱ 3.502(2), C8–O2 \cdots Cg4ⁱⁱ 75.40(14), C8–O2 \cdots Cg4ⁱⁱ 3.404(2); O2 \cdots Cg5ⁱⁱ 3.517(2), C8–O2 \cdots Cg5ⁱⁱ 82.31(14), C8 \cdots Cg5ⁱⁱ 3.561(2); Cg1 \cdots Cg4ⁱ 3.5348(13), Cg1 \cdots Cg5ⁱ 3.4527(11), Cg1 \cdots Cg4ⁱⁱ 3.7148(13). Symmetry codes: *i*) 1–x, 1–y, 1–z; *ii*) –x, 1–y, 1–z. The Cg2, Cg4, Cg5 are the centroids of the 5-membered ring C11–C20, 7-membered ring C12–C18, and 10-membered ring C11–C20, respectively. Hydrogen atoms were omitted for clarity.

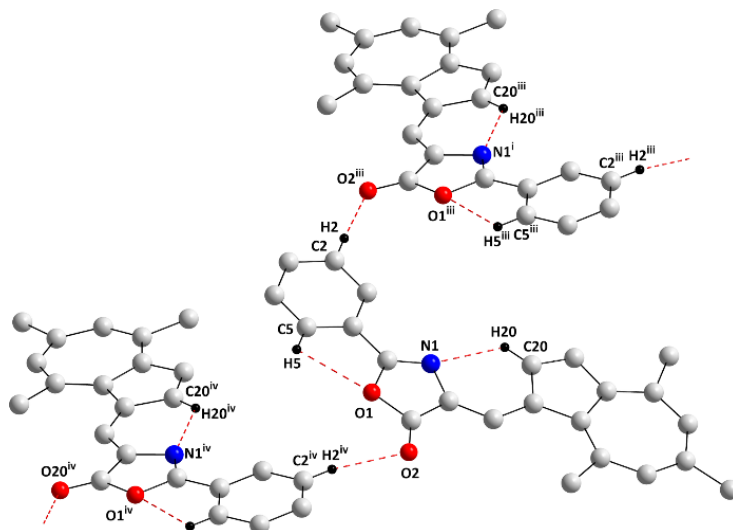


Fig. 3 – Inter- and intramolecular C–H...O or C–H...N bonds in the crystals of **1**. Hydrogen atoms not involved in interactions were omitted for clarity. Selected interatomic distances (Å) and angles (°): C2–H2 0.93, H2...O2ⁱⁱⁱ 2.51, C2...O2ⁱⁱⁱ 3.424(3), C2–H2...O2ⁱⁱⁱ 169; C5–H5 0.93, H5...O1 2.49, C5...O1 2.810(3), C5–H5...O1 101; C20–H20 0.93, H20...N1 2.39, C20...N1 2.990(3), C20–H20...N1 122. Symmetry codes: *iii*) 1/2+x, 1/2–y, 1/2+z, *iv*) –1/2+x, 1/2–y, –1/2+z.

Between the π stacked layers of molecules there are also present C–O... π contacts (Fig. 2) which augment the crystalline network along the *a* vector. Additionally, in the crystals, there are intramolecular C–H...O or C–H...N hydrogen bonds (Fig. 3) and intermolecular C–H...O bonds which afford the interconnectivity of the layers of π -stacked molecules.

The normalized contact distance, d_{norm} ,^{29,30} mapped over the Hirshfeld surface of **1** (Fig. 4) shows that the intermolecular contacts much shorter than the sum of the van der Waals radii of the

involved elements corresponds to the hydrogen bonds (highlighted in red). Although in the range of the sum of van der Waals radii (highlighted in white on the Hirshfeld surface), the π ... π interactions are significant in number in the crystals of **1**. This is also reflected in the interaction energies framework,^{30,31} which indicates that the driving forces in the crystal packing are the π ... π interactions, with an important dispersion contribution (see Suppl. Mat.) that are several orders in magnitude over the other interactions existing in the crystal (*vide infra*, Fig. 4 caption).

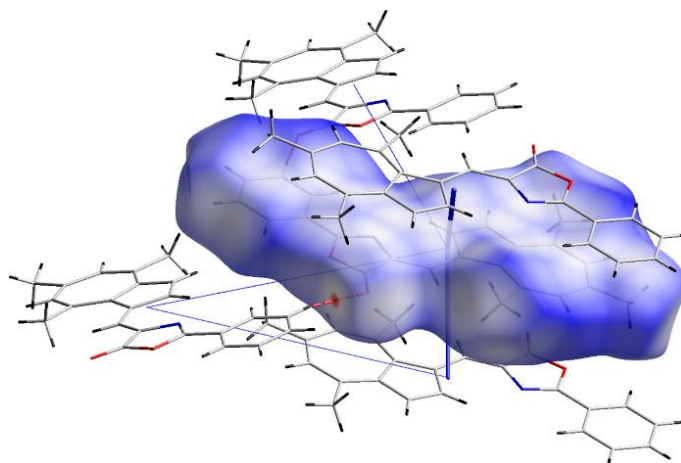


Fig. 4 – View of the Hirshfeld surface of **1** mapped with d_{norm} (–0.065 to 1.365 a.u.) overlapped with a fragment of the energy-framework diagram. The total energy is represented by blue lines. Thicker lines represent stronger interactions (*i.e.*, –92.9 and –80.9 kJ/mol) than weaker lines (*i.e.*, –18.8 and –20.2 kJ/mol).

EXPERIMENTAL

Synthesis of **1** was performed according to previous described method.¹⁷ X-ray diffraction measurement crystals was performed on a Rigaku XtaLAB Synergy-S diffractometer operating with Mo-K α ($\lambda=0.71073$ Å) micro-focus sealed X-ray tube. The crystal was kept at 293(2) K during data collection. Using Olex2,³² the structure was solved with the SHELXS structure solution program using Direct Methods,³³ and refined with the SHELXL refinement package using Least Squares minimization.³⁴ The non-H atoms were refined with anisotropic displacement parameters.

Crystallographic and refinement data for **1**: chemical formula C₂₃H₁₉NO₂; M = 341.39 g mol⁻¹; Monoclinic; P2₁/n; a = 7.0706(3), b = 18.7978(7), c = 13.7059(7) Å; β = 103.013(5)°; V = 1774.89 (14) Å³; Z = 4; D_c = 1.278 g cm⁻³; μ = 0.081 mm⁻¹; F(000) = 720; 27597 measured refl.; 4775 independent refl.; 3342 refl. with $I > 2\sigma(I)$; R_{int} = 0.040; θ_{\max} = 30.9, θ_{\min} = 1.9°; hkl ranges -10→9<-26→26, -18→19; S = 1.06; wR(F²) = 0.213; R[F² > 2 σ (F²)] = 0.073; $\Delta\rho_{\max}$ = 0.25, $\Delta\rho_{\min}$ = -0.22 e Å⁻³.

The position of the ring centroid and intra- and intermolecular interactions were evaluated with PLATON software package.³⁵ The representation of the molecular structure was carried out using Diamond.³⁶ Analysis of the intermolecular interactions was performed with CrystalExplorer.³⁰ Van der Waals and covalent radii used in the analysis were those reported by Alvarez.³⁷

Single point calculations for the CrystalExplorer model energies and energy frameworks³¹ were carried out with Gaussian 16, Revision C.01,³⁸ using the B3LYP functional,³⁹⁻⁴² and the 6-31G(d,p) 6d 10f basis set.⁴³⁻⁴⁵

SUPPLEMENTARY MATERIAL

Crystallographic data for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-2204908. Copies of the information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Tel: (+44) 1223 336 408; Fax: (+44) 1223 336 033; e-mail deposit@ccdc.cam.ac.uk; www: <http://www.ccdc.cam.ac.uk>).

CONCLUSIONS

In this article we describe the X-ray structure and Hirshfeld surface analysis of the title compound. Hirshfeld surface analysis indicates that in the crystals there are short hydrogen bonds that connect layers of π stacked molecules. Energy-framework analysis reveals that the crystal packing is dominated by the strong π interactions, which lead to column like assemblies of the molecules of **1**.

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